THE OCCURRENCE OF METHANE IN RECENT DELTAIC SEDIMENTS AND ITS EFFECT ON SOIL STABILITY

LA PRÉSENCE DE MÉTHANE DANS DES SÉDIMENTS DELTAIQUES RÉCENTS ET SON INFLUENCE SUR LA STABILITÉ DU SOL

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Summary:

River-mouth depositional pattern are modified by sediment-deforming processes of sufficient magnitude to severely endanger bottom-supported structures. Several types of deformations are present, including (a) peripheral slumping, (b) differential weighting and diapirism, (c) radial tensional faulting, (d) mass wasting and flowage induced by wave motion and degassing, and (e) deepseated clay flowage. The processes of bacterial methane production and the resulting effects on sediment deformation have been investigated in four cores taken in the Recent deltaic sediments of the Mississippi River. Dissolved methane in the interstitial waters ranged in concentration from 2×10^{-3} to 1.7 ml/l, whereas total CH_4 (dissolved plus bubble phase) ranged from 5×10^{-3} to over 300 ml l. High concentrations of methane corresponded to zones of low shear strength and were observed where dissolved sulfate was depleted. Calculations of maximum in situ methane concentrations, based on chemical reduction of excess total CO_2, indicate that methane could be present above saturation levels (bubble phase). Classical anaerobic geochemical gradients were observed in sediment profiles where no movement had previously occurred. The pore water geochemistry of sediment profiles within peripheral mudflows suggest that coexistence of methane and sulfate indicate convective mixing of sediments and bottom seawater. Calculations using the equilibrium slopes of wave-induced mudflows indicate that shear strengths during movement must be less than the values measured before or after the flow. An improved model of mass movement is presented which relates the physical and geochemical properties of unstable sediments.

Résumé:

Les structures des sédiments à l'embouchure d'un fleuve sont modifiées par des processus déformateurs d'une ampleur suffisante pour mettre gravement en danger les constructions qui s'appuient sur le fond. On peut distinguer plusieurs types de déformations: a) enfoncement périphérique; b) tassement irrégulier et diapirisme; c) formation de failles de tension rayonnantes; d) perte de masse et écoulement provoqués par le mouvement des vagues et le dégazage; et e) écoulement d'argiles profondes. Les processus de production du méthane par les bactéries et leurs conséquences sur la déformation des sédiments ont été étudies sur quatre carottes prélevées dans les sédiments deltaïques récents du Mississipi. Les concentrations de méthane dissous dans les eaux intersticielles sont comprises entre 0,002 et 1,7 ml/l, cependant que le méthane total (bulles et gaz dissous) est compris entre 0,005 et plus de 300 ml/l. Les fortes concentrations en méthane correspondent aux zones de faible résistance au cisaillement; elles s'observent aux endroits où le sulfate dissous est épuisé. Les calculs de concentrations maximales de méthane in situ, basés sur la réduction chimique du CO_2 total en excès, montrent que le méthane pourrait être présent au-dessus des niveaux de saturation (phase bulles). Les gradients géochimiques anaérobiques classiques furent observés sur des profils sédimentaires où aucun mouvement n'était apparu précédemment. La géochimie des eaux intersticielles des profils sedimentaires des coulées de boues périphériques permet de supposer que la coexistence de méthane et de sulfate indique un mélange de sédiments et d'eau du fond de la mer, par convexion. Les calculs utilisant les profils d'équilibre de coulées de boues produites par les vagues montrent que la résistance au cisaillement pendant le mouvement peut être moindre qu'avant ou après l'écoulement. On présente un modéle amélioré de mouvement de masse, tenant compte des propriétés physiques et géochimique des sédiments instables.

Introduction

Analyses of sediment borings, high-resolution seismic profiles, side-scan sonar tracks, and repeated hydrographic surveys have disclosed that a wide variety of subaqueous mass movements are active in the delta region. The major types of deformation features that have been identified include (a) peripheral faulting and slumping; (b) differential weighting and diapirism; (c) radial graben and tensional faulting; (d) mass wasting and flowage induced by wave motion and degassing; (e) deep-seated clay flowage (mud noses); (f) shelf-edge rotational slumps and normal faults; and (g) deep-seated normal faults The generalized distribution of these features is shown off South Pass in Fig. 1. A detailed description of these features has been reported by Coleman et al. (1974), Bea (1971), and Morgan et al. (1963)

These subaqueous mass movements found in the Mississippi River delta region, although complex, do have a systematic distribution (Fig. 1). All these features are of sufficient magnitude to severely endanger bottom-supported structures and pipelines and should be taken into account when bottom conditions and potential hazards are assessed.

As part of a larger study in cooperation with the U.S. Geological Survey to investigate the mechanisms responsible for the mass movements described above in the Mississippi Delta region (Suhayda, 1976; Roberts et al., 1976) chemical changes leading to gas production in modern prodelta sediments were investigated. Preservation of sedimentary organic matter associated with high depositional rates is a common occurrence near river mouths and is a necessary requirement for the generation of gas, the most important chemical parameter which affects sediment stability. The presence of sedimentary gas bubbles, primarily methane, distorts acoustical quality (Schubel, 1974; Jones et al., 1964; Hampton, 1966). High "gas porosities," an indirect measure of gas content, were observed in acoustically turbid sediments in Block 70, where bottom movements have been well documented (Sterling and Strohbeck, 1964; Bea and Arnold, 1974). It was proposed that gas accumulated in these sediments after movement had occurred and that changes in shear strengths resulted from remolding of sediments caused by movement.

Several theories have been proposed for the production of biogenic CH_4, including direct fermentation of organic matter (Koyama,

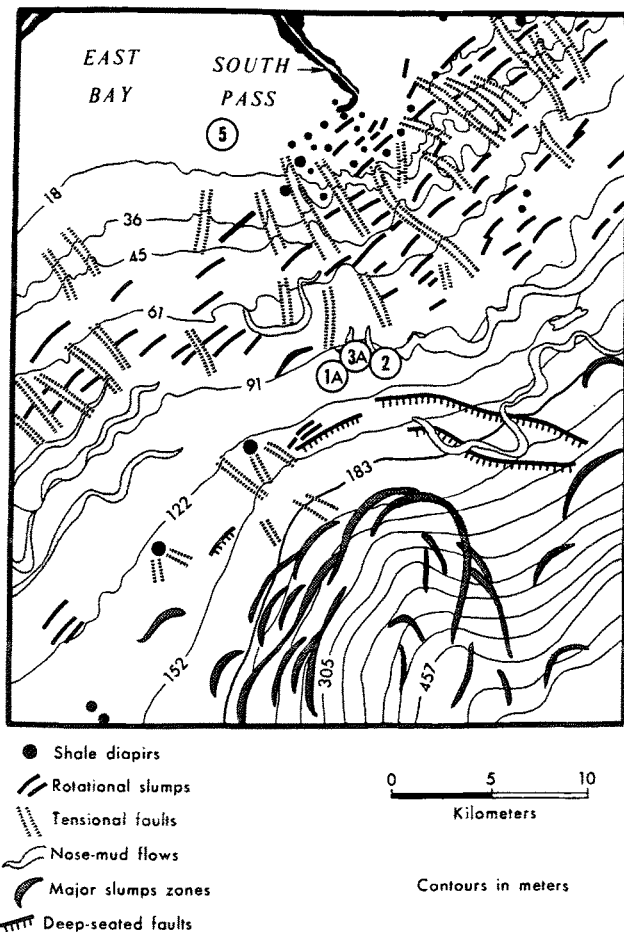* Coastal Studies Institute, Louisiana State University, Baton Rouge, Louisiana 70803, U.S.A.

Fig. 1 : Location of borings and distribution of deformational features.

added to displace all remaining air from the can, leaving only water, sediment, and a small unavoidable air space. The can lid was then pressure sealed, providing an airtight storage container until subsequent laboratory analysis. In the laboratory the sediment-water mixture within the can was shaken vigorously on a paint shaker to homogenize the sample and release any trapped gas bubbles or interstitial dissolved gas into the medium. The can was then punctured through airtight seals.

Using a stream of ultra-pure helium, the gases within the can, including methane, were purged from the can and routed through an activated charcoal trap cooled to $-77°$ C with dry ice acetone and introduced into a gas chromatograph equipped with a flame ionization detector following the procedure described by Swinnerton and Linnenbom (1967). Total methane (dissolved plus bubble phase) concentrations were determined by volume (milliliters) per kilogram of dry sediment and reported as milliliters per liter on the basis of the water content of the sediment. Replicate analysis of methane taken within the same core section indicated a $\pm 10\%$ reproducibility. Samples of $HgCl_2$-treated seawater, without sediment, were sealed periodically in the metal cans to determine procedural blanks. The average seawater methane blank of $1.89 \times 10^{-3} \pm 0.001$ ml/l was subtracted from each sample. This value was within the range reported by Brooks and Sackett (1973) for methane concentration in surface waters off the Mississippi River delta.

Results

Borehole 5 was taken in 24 meters of water and penetrated 40 meters below the mudline. This location is within a large area of poor acoustical returns. Fig. 3A demonstrates the depth distribution of CH_4. SO_4^{2-} and ΣCO_2. Dissolved SO_4^{2-} decreased from 2.1 ‰ at the mudline to less than 0.5 ‰ throughout the sequence except at 20–22 meters, where it increased to 1 86 ‰. Dissolved CH_4 ranged from 2.3×10^{-3} to 6.7×10^{-1} ml/l. The highest concentration occurred at 28.6 meters, and a corresponding decrease was noted between 18 and 24 meters.

The ΣCO_2 concentration increased from 90 to 420 mg C/1 between the surface sediment and 2.5 meters. From this point the ΣCO_2 values generally decreased with depth to about 110 mg/C/l at 40 meters. Examination of this profile on a point-by-point basis, however, indicates that generally in intervals where SO_4^{2-}. and ΣCO_2 decrease, CH_4 increases. The highest shear strengths (miniature vane values) occurred between 18 and 24 meters and corresponded to a depression in dissolved methane (see Fig. 4A).

Borehole 2 was taken in 73 meters of water and extended to a depth of 61 meters below the mudline. Bathymetry and sub-bottom acoustic data indicate this to be a zone of downslope peripheral mud flowage.

The high-resolution profile taken across BH2 was characteristic of acoustically turbid sediments. Sedimentary structure was discernible only at intermittent intervals along the profile (Fig. 2). Total CH_4 concentrations (Fig. 5) above 30 ml/l began at 5 meters below the sediment-water interface and continued to below 53 meters. Geological inspection of the samples taken from this boring did not show a shell hash zone or any significant sedimentary structure. An X-radiograph (Fig. 6A, 17 meters) illustrates large, randomly oriented gas structures within a homogeneous clay matrix. Fig. 6B (58 meters), at the base of the high-gas/low-strength zone, depicts microfracture planes in fine-grained stratified sediment lying directly below a gas-charged zone (top of radiograph). The dissolved species of the interstitial waters in Fig. 3B follow a pattern similar to that found in BH5. Dissolved SO_4^{2-} decreases from 2.6 ‰ at the mudline to 0.6 ‰ at 1.2 meters and remains below 0.7‰ to the bottom of the core. Dissolved CH_4 ranges from 4.3×10^{-3} ml/l in the surface sediment to 1.2 ml/l at 17 and 26 meters. In general, ΣCO_2 is higher in scattered intervals where SO_4^{2-} is decreasing. As in core 5, no consistent gradient exists in the depth distribution of these dissolved species. Methane is uniformly high and may fluctuate 0.8 to 1.0 ml/l within a 5-meter interval, whereas shear strength values (Fig. 4B), ΣCO_2, and SO_4^{2-} are relatively low.

Borehole 1A (101-meter water depth and 54-meter penetration) was taken due west of borehole 2 in an area of relatively well defined sedimentary strata above 10 meters. Acoustic reflectors were observed to a depth of approximately 13 meters below the sediment-water interface. Between 13 and 40 meters no acoustic

1964) and biochemical reduction of preformed CO_2 (Nissenbaum, 1972). Methane accumulation in anoxic marine sediments occurs only after dissolved sulfate has been depleted by way of biochemical reactions generating sulfide and bicarbonate. The interstitial water geochemistry associated with methane production has been investigated in several nearshore environments; the majority of the samples were taken no deeper than 10 meters below the sediment-water interface (Nissenbaum, 1972; Martens and Berner, 1974; Whelan, 1974; Presley and Kaplan, 1968). Claypool and Kaplan (1974) reported methane distributions and associated interstitial water geochemistry in deep-sea sediments extending several hundred meters below the mudline from selected worldwide localities. In each environment, however, methane concentrations become significant only if a sufficient amount of sedimentary organic matter is present (anoxic sediments) and after the dissolved sulfate is depleted. The purpose of this report is to present results from a study of methane distribution and interstitial water geochemistry in modern sediments of the Mississippi River delta province which suggest that the presence of sedimentary gas may account for changes in shear strength with depth.

Methods

Core locations were chosen on the basis of 3.5 kHz sub-bottom profiler data (Garrison, 1974). Borehole BH1A was taken in a zone of good surface reflectors, BH3A was taken within a zone of poor but discernible reflectors, and BH2 and BH5 were taken in sediments with no acoustic reflectors (Fig. 2).

Sediment shear strengths were determined on board ship from a miniature vane. The sediment sampling procedure, interstitial water analysis, and actual shear strength data have been presented by Whelan et al. (1975).

Sediment samples were taken directly from the core barrel in liners and quickly extruded into a metal can which had been partially filled with degassed, Hg_2Cl_2-treated seawater. Sufficient sample was
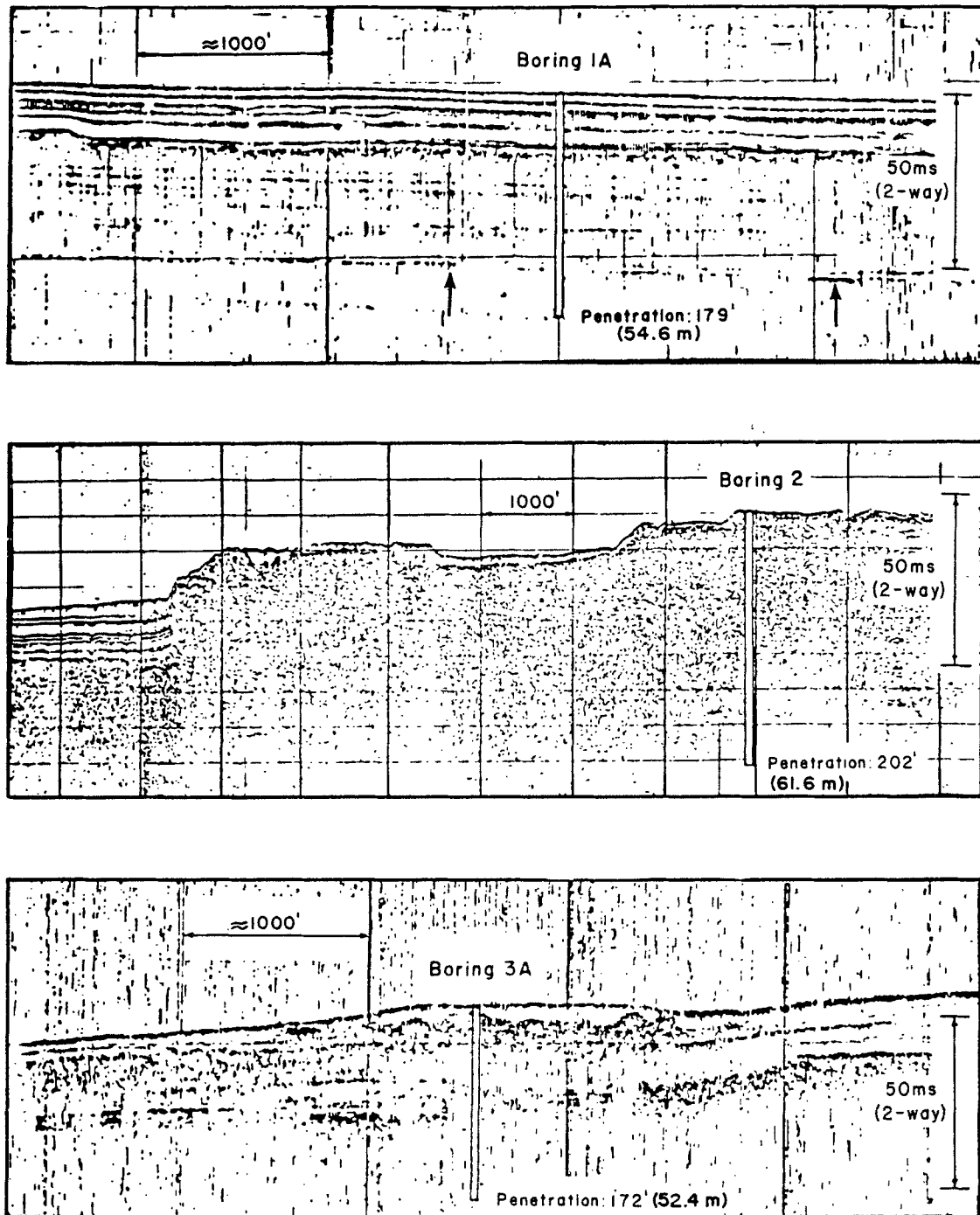
Fig. 2 : Sub-bottom profile (3.5 kHz) across the regions of BH1A (arrows indicate shell hash), BH2, and BH3A.

reflectors appear. This corresponds to the zone of highest methane concentration within this borehole (Fig. 7). Geological inspection of the boring indicated a thin (15 cm) shell hash at 40 meters below the mudline. Methane concentrations from the shell hash to the end of the boring were close to background levels. Apparently the gas content in the 26-meter zone above the shell hash was sufficient to absorb or scatter acoustical energy such that returns below the high gas zone, except from the shell hash, were not obtained. There is no geologic evidence for recent movement of this sedimentary sequence. The depth profile (Fig. 3C) of dissolved species is significantly different from that of either BH5 or BH2. Dissolved SO_4^{2-} decreased from 1.65 to about 0.4‰ at 11 meters, and a concurrent increase occurred in CH_4 from 4 x 10^- to 1.2 ml/l. Total CO_2 concentration decreased from 460 to 120 mg C/1 between 11 and 14 meters. Dissolved CH_4 remained consistently high between 11 and 28 meters, and SO_4^{2-} and ΣCO_2 were consistently lower within this interval. It should be noted here that acoustic reflection

is lost between 11 and about 40 meters (Fig. 2). an area which corresponds to the zone of high total CH_4. Shear strength of this core is consistently higher than that of the previous two, especially below 34 meters (Fig. 4C). Borehole 3A was taken in 85 meters of water to a depth of 52 meters below the sediment-water interface. Erratic, low-quality returns were obtained from the sediment-water interface to about 11 meters. Total methane concentrations in this top 11 meter section ranged from 5 x 10^{-3} to 30 ml/1 (Fig. 8). Below 11 meters no acoustical returns were obtained. Methane concentrations between 11 and 33 meters ranged from 30 to 78 ml,1, respectively. A shell hash zone presumably contiguous with the boring observed in BH1A occurred at 43 meters below the sediment-water interface. No discernible acoustic reflector appeared at this depth. In BH1A, where methane concentrations above 30 ml/1 occurred from 13 to 90 meters, the shell hash was faintly observed on the acoustic record. Methane concentrations above 30 ml/1 in BH3A, however, occurred from 8 to 38 meters. Thus, the
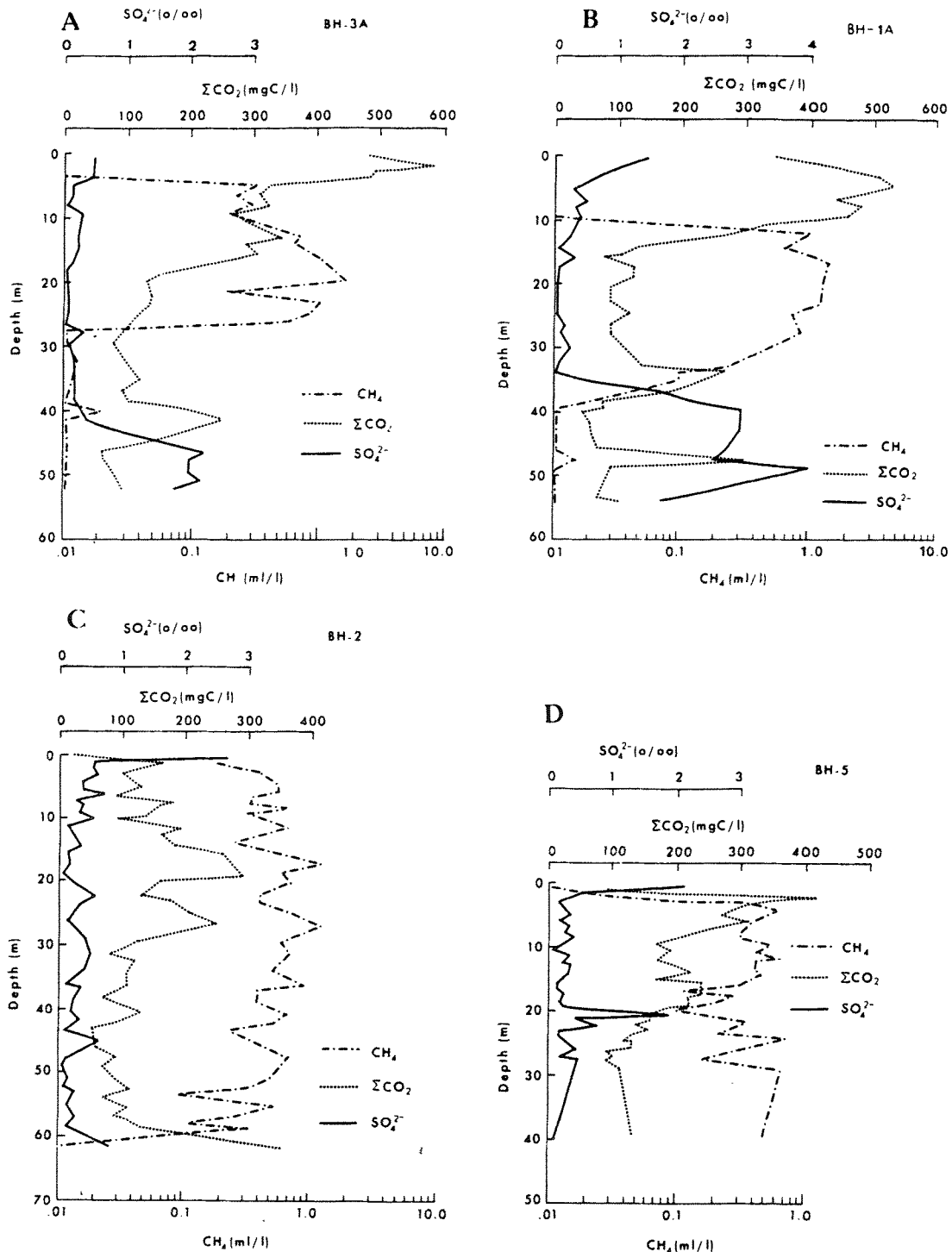
Fig. 3 : Concentration profiles for dissolved species in interstitial water from BH1A, 2, 3A and 5.

thickness of gas-charged sediment (above 30 ml/l) in BH3A was about twice that of BH1A and could possibly account for the complete masking of the shell hash.

The pore water profile is similar to that of 1A: When SO_4^{2-} went below about 0.5‰. at 5 meters, dissolved CH_4 increased from 1.3×10^{-2} to a maximum of 1.7 ml/l at 20 meters (Fig. 3D). Total CO_2 decreased from 590 mg C/l at 1 8 meters to 80 mg C/l at 29.3 meters, an interval which was consistent with the zone of higher methane concentrations. Several sedimentary sequences were observed in this core. Well-stratified red, green, and gray clays were present below about 38 meters. The beginning of this sequence is shown in the radiograph (Fig. 9A). Distinct laminar, well-con-

solidated clays appear at this interval as opposed to the porous gas structure observed in this core (Fig. 9B) at 7 meters below the mudline. Shear strength consistently increased from 0.4 KIPS at 35.4 meters to 0.65 KIPS at 50.6 meters (Fig. 4D). Within this same interval, SO_4^{2-} increased and CH_4 dropped to background levels. This set of conditions is consistent with the theory that this interval represents a geologic period when depositional rates were much slower and organic matter preservation was less; thus anaerobic respiration was suppressed and high levels of dissolved SO_4^{2-} and low levels of CH_4 were maintained.

The data in Table 1 demonstrate shear strength and gas concentrations from three units of boreholes 2, 3A, and 1A. Consideration of
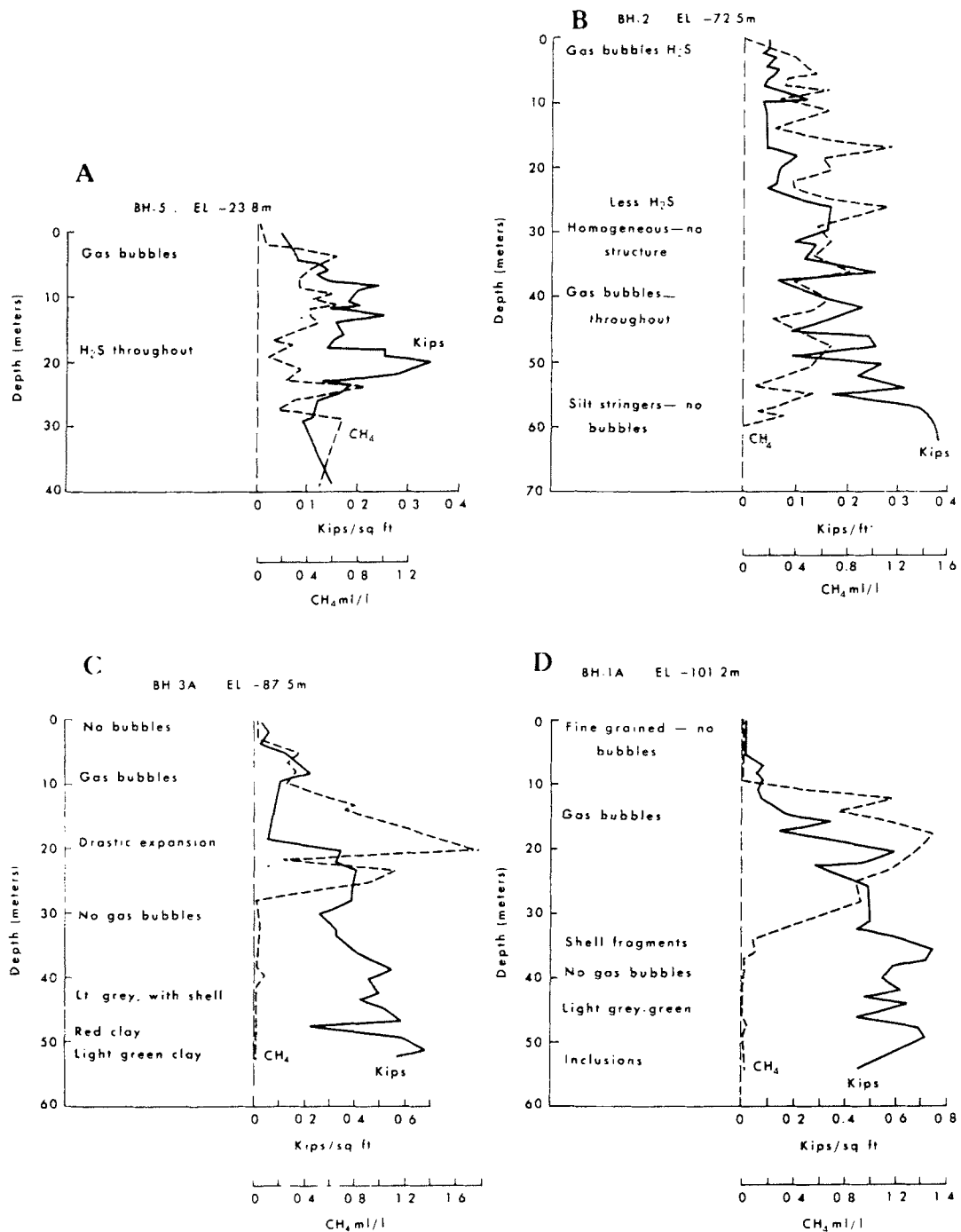
Fig. 4 : Depth distribution of dissolved methane and shear strength.

BH5 was omitted because of a lack of suitable sub-bottom profiles. The surface reflector zone includes data from those samples which were taken in the zone of good reflectors in BH1A and poor but discernible reflectors in BH3A. The mid-depth acoustically turbid zone includes regions beginning the loss of surface reflectors (also beginning of increased gas content) to a transition in sediment types marked by a shell hash zone or a drastic change in sediment depositional environment. Borehole BH2 is listed only in the acoustically turbid zone since no acoustic reflectors were present, no change in sedimentary structure occurred, and gas concentration was significant throughout the core.

The fractional change in shear strength per unit depth in each of the three sedimentary-acoustic zones indicates that the smallest increase in shear strength with depth occurred within the mid-depth acoustically turbid zone (Table 1). In addition, this region of the

sediment column, in each borehole, had the highest average methane concentration.

Discussion

Sediments of the Mississippi River delta which demonstrate acoustically impenetrable or "turbid" zones correspond to those sediments which contain quantities of methane gas above approximately 30 ml(STP)/1. Examination of the sedimentary structure by X-radiography indicated that gas expansion features were present at depth intervals where acoustically turbid returns and high methane values were obtained. Thus, if gas bubbles were present in these sediments at atmospheric pressure, then a certain amount of gas was likely lost during the sampling procedure. Without a pressurized sediment sampling device, capable of maintaining in situ pressures (10–20 atmospheres in this study)
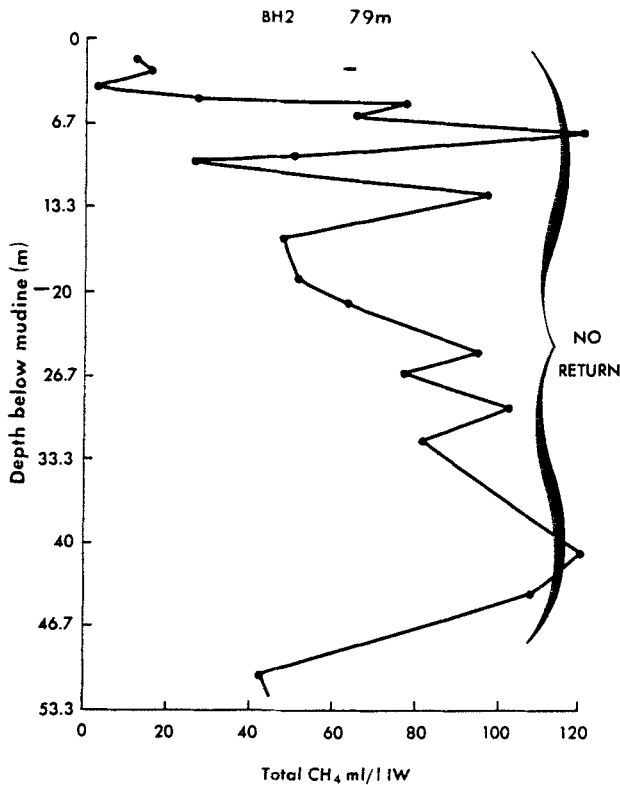
BH2   79m

Fig. 5 : Concentration profile of total CH₄ (dissolved plus bubble phase) demonstrating no acoustical returns.

until analysis, methane gas measurements are, at best, minimum values. The reproducibility of ± 10 % was estabilished in both high and low gas zones, and the correlation coefficient between dissolved and total CH₄ was 0.84, thus the gas loss error was reasonably systematic.

Results from recent investigations of methane production in shallow-water sediments (Martens and Berner, 1974; Whelan, 1974) and in deep-sea sediments (Claypool et al., 1971) indicate that methane accumulates only after dissolved sulfate is removed by sulfate-reducing bacteria. Theoretical considerations of energy-yielding microbial succession models support these observations (Nissenbaum et al. 1972; Mechalas, 1974; Claypool and Kaplan, 1974). That is, aerobic respiration is the most energetically favorable process; next is anaerobic sulfate reduction; then comes CO_2 reduction to methane. The results from BH1A and BH3A indicate this sequence of processes Dissolved sulfate is depleted to an average of 0.13 and 0.17‰ in BH3A and BH1A, respectively, within zones where methane is present above background levels (Table 2). In contrast, average sulfate concentrations in BH2 and BH5 are 0.30 and 0.31‰, respectively, where methane appears (essentially throughout the sequence). Thus an explanation must exist for the coexistence of methane and relatively high values of sulfate in BH5 and BH2. One explanation is that metabolic processes regulating sulfate reduction and methane production in BH1A and BH3A are determined by burial and diffusion of dissolved pore water species (classical ecological succession), whereas the processes regulating sulfate and methane in BH2 and BH5 are complicated by convective mixing of bottom seawater and sedimentary material associated with bottom movement. Convective mixing, caused by downslope movement, would yield isolated sulfate-rich zones that would be surrounded by methane-generating sediments. Methane production in these zones would temporarily cease until sulfate was
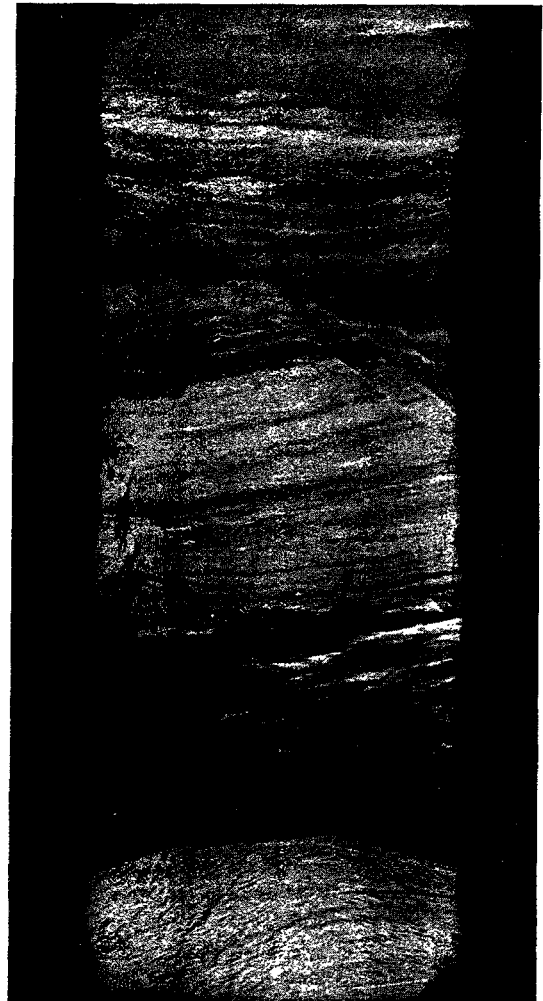

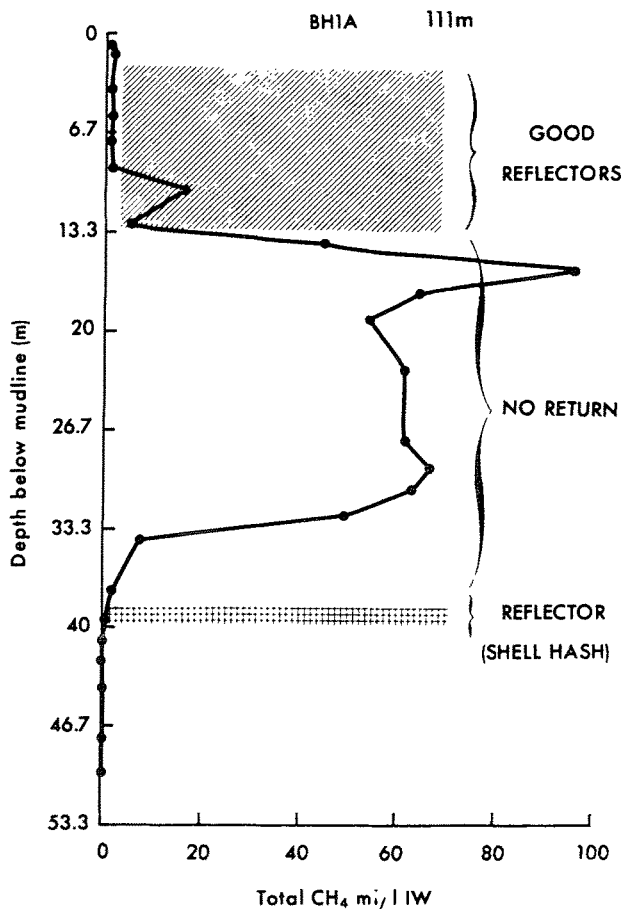Fig. 6 : X-radiographs taken from 19 meters (A) and 64 meters (B) below the sediment surface in BH2.

Fig. 7 : Concentration profile for total methane, illustrating section of various acoustical quality in BH1A.
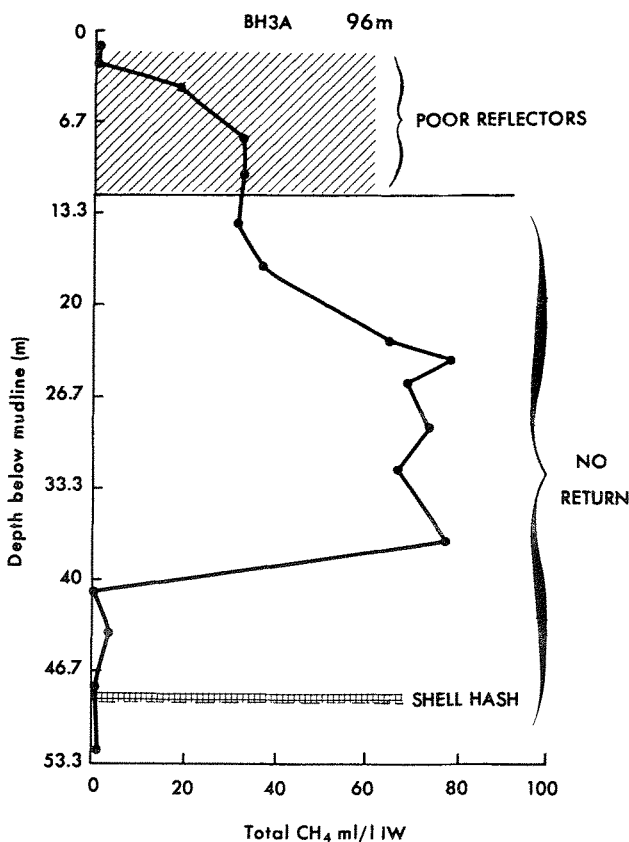

Fig. 8 : Concentration profile for methane in BH3A illustrating section of various acoustical quality.

depleted to a tolerable level (apparently below about 0.15 ‰ or 1.6 mmoles l^{-1}). The vertical distribution of dissolved species would be erratic, as observed in BH2 and BH5, and dramatic concentration fluctuations would occur within an interval of a few meters. This concept suggests that the influx of bottom seawater into the sediment, owing to convective mixing associated with downslope flowage, would temporarily inhibit gas -production rather than accelerate it, as suggested by Bea and Arnold (1973). The presence of sedimentary gas is a causative factor rather than a result of bottom movement.

Even though special precautions for sampling dissolved methane were taken, the absolute values are much lower than would be expected for in situ dissolved methane concentrations (Reeburgh, 1969; Martens and Berner, 1974; Whelan, 1974). The relative concentrations are, however, reasonable when the relationship between methane and dissolved sulfate is considered. An upper limit of methane concentration can be estimated from the data in Table 2. During microbial sulfate reduction, each molecule of sulfate degraded should yield 2 molecules of bicarbonate according to the reaction

$$2 [CH_2O] + SO_4^{2-} \rightleftarrows 2HCO_3 + HS^- + H^+$$
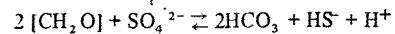
The measured average ΣCO_2 is 2–3 times less than predicted from this equation. Presley and Kaplan (1968) determined that the excess ΣCO_2 from nearshore sediments where methane production was apparently not active was about 2 1/2 times greater than could be accounted for by sulfate reduction processes alone. Thus, if it is assumed that the reduction in ΣCO_2 levels from the theoretical maximum is due to methane production, according to the reaction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O ,$$
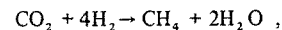
then up to 658.5 ml/l^{-1} of methane could have been produced in BH1A. Satisfactory values for pressure dependence on the solubility of methane in seawater are not available. Emery and Hoggan (1958) reported dissolved methane concentrations up to 10.4 mmole kg^{-1} (233 ml/l^{-1}) for Santa Barbara Basin sediments in about 600 meters of water. Thus, if this value is an upper solubility limit for dissolved methane at 60 atmospheres pressure, each core could have produced methane above saturation levels (in the bubble phase).

An idealized model of respiratory processes in marine sediments is shown in Fig. 10 (from Claypool and Kaplan, 1974). In the aerobic zone, oxygen is the active dissolved species. As oxygen becomes depleted, anaerobic respiration becomes dominant, and sulfate reduction processes yield excess ΣCO_2 (lower pH to about 7.2) enriched in ^{12}C with respect to seawater. The redox potential, regulated primarily by the rate of removal of the S^{2-}ion, generally falls below -200 mv. When sulfate is depleted, CO_2 reduction is the next most energetically favorable respiratory process. Redox potential is highly variable and may be as high (positive) as found in the aerobic zone owing to the lack of continual generation of H_2S. Nissenbaum et al. (1972) suggest that redox potential is controlled by the solubility of metal oxides or carbonates. Microbial CO_2 reduction favors reaction of the lighter ΣCO_2 molecule, and the result is a pool of ΣCO_2 which is depleted in ^{12}C with respect to the sulfate-reducing zone.

The pore water geochemistry from deltaic sediments in this study indicates that the aerobic zone is negligible and that sulfate is reduced rapidly with depth. The methane-producing zone is extensive and, in the case of BH1A and BH3A, lithological changes in sediment type below this zone account for the decrease in methane and increase in sulfate. This process corresponds to the slow sulfate-reducing zone where the rate of microbial processes is controlled by the diffusion of organic carbon into this zone.

The relationship between gas concentration and shear strength changes suggests that wave-induced bottom pressure fluctuations may lower shear strength by releasing or expanding bubbles from solution in the pore waters. There is evidence that large changes in shear strength associated with bottom movement have occurred. The best documented slide occurred in Shell Oil Company's South Pass Block 70 (Sterling and Strohbeck, 1973). Premovement shear strength profiles exhibited a crust-type profile. Significant shear strength changes were observed within the upper 21 meters; however, not all borings in the area of flowage showed equal reductions. This result may indicate that remolding caused by flowage is not the only explanation for shear strength changes. In this area, reduction in shear strength after movement was as high as 80 %. High gas porosities, an estimate of void space, were observed
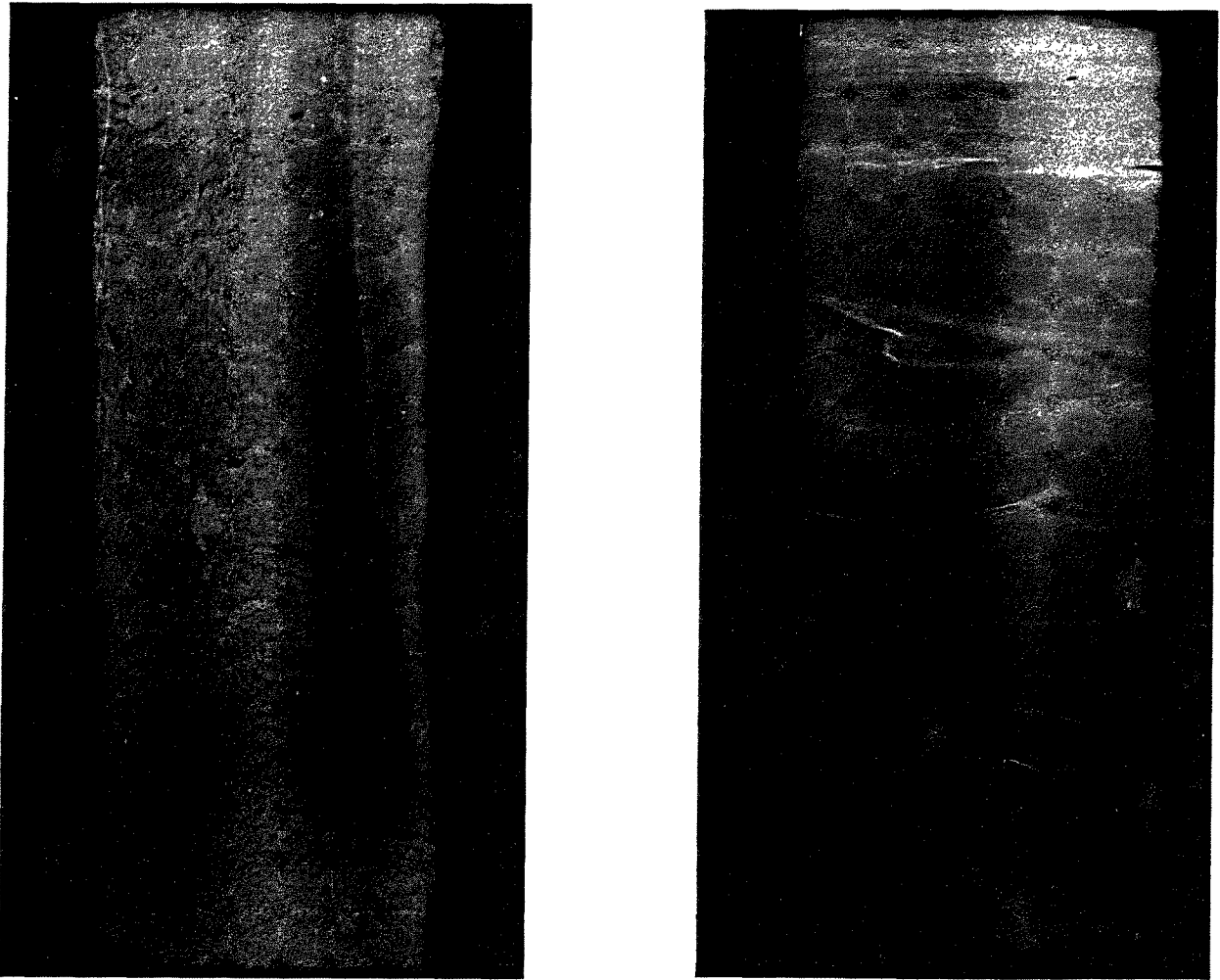
Fig. 9 : X-radiographs of porous gas filled sediment at 7 meters (A) and well-consolidated, firm clays at 43 meters (B) in BH3A.

Parameter	Surface Reflector Zone			Mid-Depth Acoustically Turbid			Transition Zone		
	BH1A	BH3A	BH2	BH1A	BH3A	BH2	BH1A	BH3A	BH2
Thickness (meters)	13	11	–	27	69	50+	13	12	–
Ave. Gas Concentration (ml/l)	2.3	17.2	–	51.9	56.5	64.9	.05	.69	–
Ave. Shear Strength (KIPS/ft^2)	.056±.001	.089±.002	–	.39±.003	.34±.001	.11±.002	.59±.004	.51±.003	–
Shear Strength Range	.020-.088	.030-.23	–	.24-.57	.27-.57	.028-.26	.42-.75	.23-.66	–
Fractional Change in Shear Strength per Unit Depth	.085	.17	–	.017	.005	.055	.032	.053	–

Table 1: Classification of Sediment Strength, Gas Content, and Acoustical Characteristics from Three Foundation Borings

in zones of low shear strength. Actually, shear strengths might be expected to increase slightly as sediments consolidated after movement. The implication is that lower shear strengths may have existed than those measured after movement. An estimate of the lowest shear strength value can be made from the equilibrium slope of the displaced sediment. Assuming that movement stopped when gravitational shear forces were balanced by sediment shear strength, the ratio of shear strength of immersed pressure would be equal to the bottom slope (Henkel, 1970). The slope was approximately 0.005, a value which implies that a minium shear strength of 0.006 TSF occurred at 18 meters below the mudline. This value is about one-fifth of that of the shear strength measured after movement (0.03 TSF at 18 meters).

An improved model of mass movement may be described which relates the physical and geochemical properties of unstable sediments (Fig. 11). Rapid deposition of fine-grained, organic-rich sediments yields the classical anaerobic geochemical gradient within the sedimentary column. Sulfate reduction is dominant in upper zones, and no methane accumulates. This zone has the same depth dimensions as observed in the "crust zone" of typical deltaic shear strength profiles. After sulfate has been depleted, carbonate reduction begins and methane increases in concentration to a point where bubbles form and shear strengths are lower than in the zone directly above (failure zone). Methane decreases with depth from some point where carbon becomes limiting (transition zone) owing to a change in lithology. The basement zone corresponds to a depositional

	Average* SO_4^{2-} (mmole l^{-1})	Average ΣCO_2 (mmole l^{-1})	Theoretical Excess ΣCO_2 (mmole l^{-1})	$\Delta \Sigma CO_2$ (mmole l^{-1})	Theoretical CH_4 (ml l^{-1})
BH5					
Surface	3.3	15.5	33.0	17.5	392.0
Seawater	19.8	4.2			
BH2					
Surface	3.1	10.8	34.6	23.8	533.0
Seawater	20.4	4.2			
BH1A					
Surface	1.8	13.2	42.6	29.4	658.5
Seawater	23.1	4.2			
BH3A					
Surface	1.3	22.3	42.8	20.5	459.2
Seawater	22.7	4.2			

*Averaged within zones where CH_4 was above background levels.

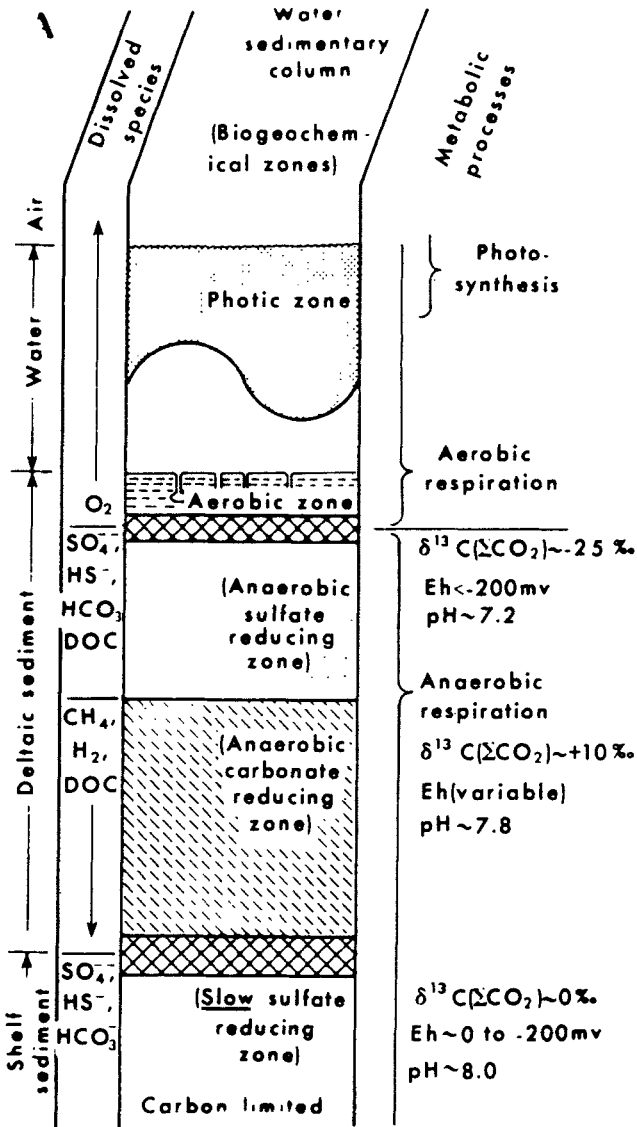Table 2: Carbon Budget for Methane Production from Chemical Reductive Processes

Fig. 10 : Idealized model of respiratory processes in marine sediments (modified from Claypool and Kaplan, 1974).

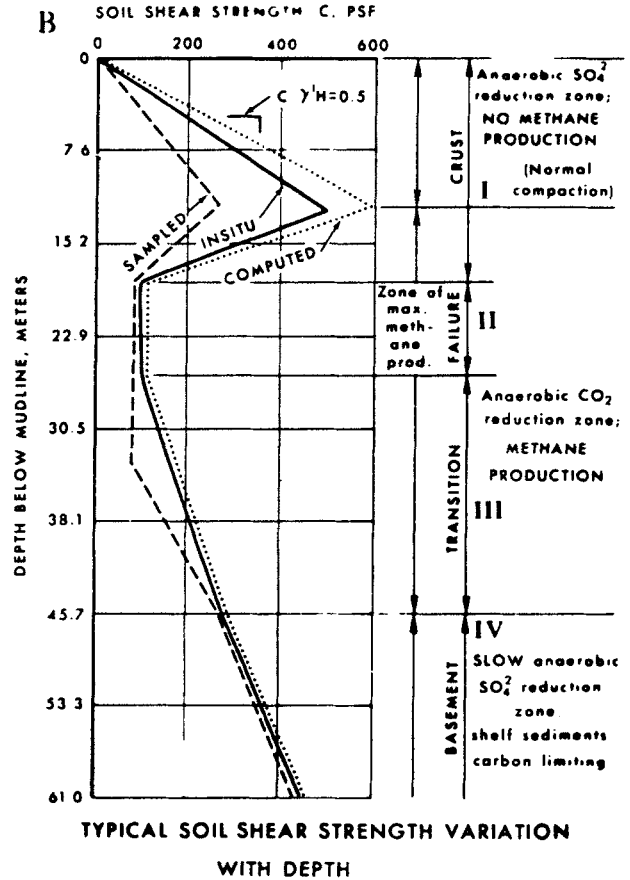**TYPICAL SOIL SHEAR STRENGTH VARIATION WITH DEPTH**

Fig. 11 : Typical shear strength profile modified to include geochemical mechanisms.

environment where sulfate reduction is operating at a slow rate.

Bottom pressure fluctuations caused by storm waves or longperiod surface waves allow gas bubbles to migrate upward (cyclic or otherwise) toward the sediment-water interface. This process lowers shear strength from the failure zone upward. Movements, especially downslope, occur at the time of lowered shear strength (gas ebullition), which may be occurring before maximum wave action.

During bottom movement, convective mixing of sediment and renewed seawater replenishes sulfate and terminates methane production. Coexistence of methane and sulfate occurs within microenvironments of the sedimentary column. Anaerobic respiration begins at discrete zones within the disturbed sediment until all sulfate is again depleted. Thus an erratic distribution of dissolved species is observed in the interstitial waters, and the classical geochemical gradient is destroyed.

At some time after movement, shear strength in the failure zone and above are uniformly lower than before movement. Lowering of shear strength is, in part, due to remolding by the release of gas bubbles. The crust zone loses its identity because gas is now present in the previous zone of sulfate reduction.

Conclusions

1. Significant differences exist between the geochemistry of deltaic sediments which have moved and those which have not.

   a) In zones which have been subjected to movement, methane concentrations are high, and fluctuations in both shear strength and dissolved species (BH2 and BH5) are erratic. Microenvironments are created by convective mixing of sediment and seawater, and coexistence of dissolved sulfate and methane occurs.

   b) In zones where no movement has occurred, a classical profile of anaerobic respiratory processes is observed. Methane production and sulfate reduction are mutually exclusive processes. Rates of reaction are determined only by diffusion of dissolved species into and out of the sedimentary column (BH1A and BH3A).

2. An improved model of mass movement has been developed which relates the physical and geochemical properties of potentially unstable sediments.

3. The percentage increase in shear strength with depth of overburden was minimized in the high-gas, acoustically turbid zones.

Acknowledgments

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